GC

AND THE COFFEE CRISIS

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Whatever brew strikes your fancy, GC can ensure its flavor and healthfulness—and it may also help save the global coffee economy.

From the opening of the first English coffeehouse in 1650 in the city of Oxford, the Western palate has been obsessed with this caffeinated concoction. Originally, the flavor and quality of coffee depended on the discriminating ability of employees of each coffee company. Their experience in buying and mixing coffee as well as roasting beans meant that coffee taste and texture were reproducible—at least as far as the consumer knew. But with the explosion of coffee consumption in recent years, and the growing sophistication of the consumer, the noses of old employees have had to be augmented with the latest science and analytical chemistry.

Although modern coffee is grown around the world, it is originally a native of Africa. The quality of this beverage has become an ever more important issue as its global market implodes and changes. For although coffee is second only to petroleum in commodity trading, and despite the fact that its growth and production provide employment for nearly 20 million, coffee production today is in crisis. Prices have dropped more than half since 1998, with the 2003 price per pound being the lowest in a century (*1*).

Providing a more competitive product is one of the few hopes for bolstering coffee prices without global subsidies. A less desirable alternative is to allow or create a collapse of the market, which would lead to more unemployment and chaos in developing nations in Central and South America, Africa, and Asia (where Vietnam has become the chief provider of cheap coffee due to its low labor costs). According to the U.S. Agency for International Development (USAID), "Where potential exists for farmers to effectively compete within the coffee sector, USAID is working to improve local capacity to produce and effectively market high-quality coffee, thereby increasing the price farmers earn for their product" (*2*).

In the effort to ensure reproducibility and objectivity in the process, traditional human "taste testers" are slowly giving way to (or at least are being supplemented by) analytical instrumentation.

In particular, GC may have a critical role in the future of global coffee production as one of the best monitors of flavor quality and composition available. Because of this profound new demand for quickly and objectively assessing quality in a market glutted with cheap and less desirable beans, GC may be an important tool in "saving" significant numbers of coffee producers from bankruptcy, if not the coffee market as a whole.

Coffee Perfection

Flavor is perhaps the most important consideration in coffee quality. It is also one of the most variable components of coffee beans. Flavor can be influenced by the species, the processing of the green coffee bean, the roasting method, and the method of brewing (see box, "Coffee Cacophony").

Because the coffee market is so volatile, companies with specific flavor brands have a need to maintain the taste, if not the bean composition, of their varieties so as to provide the consumer with

COFFEE BEAN AND BAG PHOTO: PHOTODISC; ILLUSTRATION: TONY FERNANDEZ

a consistent product. This leads to "flexible blending"—the mixing of coffee obtained from different sources to achieve a standard taste. As sources change because of pricing and availability, they may be unpredictably flavored due to the abovementioned variables, and it becomes a problem in chemical analysis to mix them to provide an ultimately consistent product.

Traditionally, a panel of trained tasters evaluates the blended coffees in what is known as organoleptic analysis, but many now consider this insufficiently objective. According to Inge Dirinck of Catholic Technical University St. Lieven, Gent, Belgium, "Objective methods for characterizing coffee flavor become necessary in today's international coffee trade and production. . . . Chemical-analytical profiling—e.g., gas chromatography-mass spectrometry (GC-MS), high-pressure liquid chromatography with UV detection (HPLC-UV), chemical sensor technology, titratable acidity—can give an unbiased characterization of a coffee variety."

In this research, Dirinck examined the volatile compositions of 10 arabica and 7 robusta coffees using simultaneous steam distillation extraction-gas chromatography-mass spectrometry

(SDE-GC-MS). Arabica and robusta species could be distinguished using phenolics as the most discriminating aroma compounds, allowing predictions concerning interchangeability of coffee varieties with regard to "flexible blending." Dirinck reported that the predictions were supported by traditional sensory data and chemical titration of acidity (*3*).

In a follow-up applications note with colleagues, Dirinck demonstrated that the "classical" SDE-GC-MS method proved time-consuming (4 h per coffee sample for the SDE alone) compared with the use of an "electronic nose," an automated static headspace-chemical sensor (S-HS-Chem-Sensor [Gerstel, Baltimore]) consisting of a GC-MS system with a multipurpose sampler and pattern recognition software (which performed the analysis in 1 h per coffee sample) (*4*).

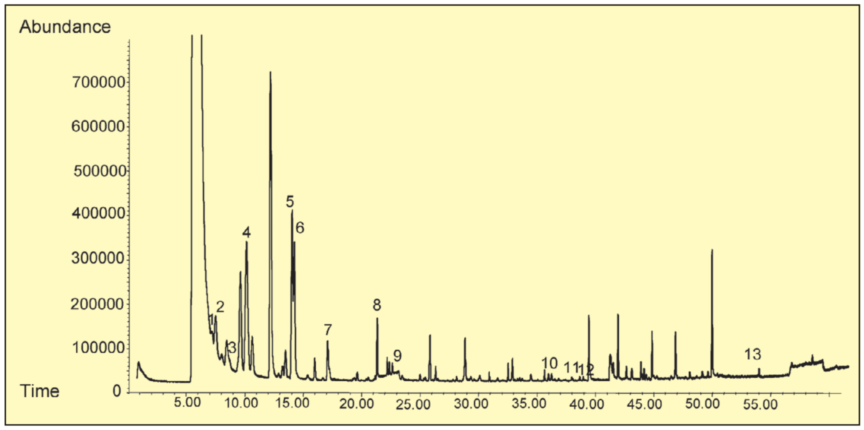

Figure 1. GC-MS chromatogram of volatile compounds from espresso coffee. Identification of key odorant peaks: (1) methanethiol, (2) acetaldehyde, (3) propanol, (4) 2-methypropanol, (5) 2-methylbutanol, (7) 2,3-butanedione, (8) 2,3-pentanedione, (9) hexanol, (10) 2-ethylpyrazine, and (11) 2-ethyl-6-methylpyrazine. (Adapted with permission from Andueza, S.; et al. *J. Agric. Food Chem.* **2003,** 51, 7034–7039.)

A Volatile Situation

As might be expected, postbrew heating has a profound effect on the flavor of coffee. Japanese researchers Kenji Kumazawa and Hideki Masuda, at Ogawa and Company, used GC-olfactometry of headspace samples to examine the vapor fraction before and after heat processing of canned arabica coffee-drink samples. They detected 12 odoriferous peaks for which the flavor-dilution classification changed on the basis of subjective analysis by trained taste-test subjects. Eight of these peaks were identified using GC-MS. Components giving sour, putrid, meaty, and caramel-like scents increased, while odorants giving roasty and potato-like scents decreased (see Table 1) (*5*).

In another case where flavor analysis is being turned to the improvement of coffee quality, Indian researchers are attempting to find ways to preserve and qualify the high-quality "monsooned coffee," a specialty coffee with a characteristic taste and aroma that command that country's highest market prices.

Monsooning is a process whereby dry raw coffee beans are exposed to moist monsoon winds, nearly doubling the moisture content of the beans and their size. Such long-term exposure to natural conditions has plagued these beans with insect infestation and microbial contamination, reducing their shelf life considerably. Attempts are under way to use radiation processing rather than chemical fumigants. Researchers P. S. Variyar and colleagues at the Food Technology Division, BARC, Trombay, and Mangalore University, Mangalagangotri, India, analyzed monsooned and nonmonsooned aroma compounds using GC-MS and determined the most potent odorant compounds were the same in both samples, but that a decrease in methoxypyrazines and an increase in 4-vinylguaiacol and isoeugenol resulted in the dominant spicy quality of monsooned coffee. These latter compounds were released from their bound glycosides during the monsooning process. The changes were attributed to enzymatic processes rather than chemical degradation.

Radiation treatment, while not affecting these parameters, increased the hydrolysis of chlorogenic acid to caffeic acid whether carried out before or after monsooning. This was a potential problem because such a shift has been known to increase the bitterness of coffee (and is, in fact, responsible for much of the bitterness found in coffee left too long on a hot plate) (*6*).

Not only volatile aromatic flavoring compounds are useful for determining source differences in coffee beans. Researchers Susana Casal and colleagues at the University of Porto (Portugal) found that they could differentiate species through examining the amino acid enantiomers present in both the green and roasted states. The amino acids were extracted, hydrolyzed, and isolated by solid-phase extraction on a strong cation-exchange column,

Coffee Cacophony

A cup of coffee can be characterized by its odor, acidity, bitterness, astringency, flavor, body, and aftertaste. Each one of these components is based on a human sensory response that is increasingly being matched to chemical and analytical analysis. There can, unfortunately, be no fixed solution to the problem of creating the perfect cup of coffee by selecting the perfect coffee bean, the perfect roast, the perfect grind, and the perfect brewing technique. Not only do human tastes vary in defining what such perfection would be (consider the purist espresso lover confronting the triple mocha latte with chocolate sprinkles), but the biology of the coffee plant and coffee bean varies with soil, climate, and cultivar—much less species.

The favored species *Coffea arabica* var. *arabica* is the most popular; seed that was originally obtained from African-origin plants grown at the Amsterdam Botanical Gardens accounts for most of the billions of plants in Central and South America and the Caribbean today. A French strain obtained from Réunion Island in the Indian Ocean accounts for the other important arabica variety, *bourbon*. The oft-considered lower-quality robusta coffee is actually from a different species, *Coffea canephora*.

The ultimate goal of using analytical instrumentation such as GC to sort this cacophony is to create a series of standards by which every taste could be reproducibly satisfied by the appropriate blends, treatments, and selections, using objective criteria. For example, a large number of detectable volatiles are seen in GC-MS of espresso (see Figure 1).

derivatized to their *N*-ethoxycarbonylheptafluorobutyl esters, and analyzed using GC/flame ionization detection.

Multivariate analysis showed that arabica and robusta could be differentiated on the basis of the derived pattern, particularly with regard to L-glutamic acid, L-tryptophan, and pipecolic acid. Such a technique provides another potential way to determine whether coffees have been adulterated on the market, and, according to the researchers, it may also one day be adapted to determining specific geographical sources (*7*).

Interest in improving the quality of coffee is not restricted to flavor analysis. Recent observations that coffee contains powerful antioxidants that may have a health-promoting effect led researchers Kenichi Yanagimoto and colleagues at the University of California, Davis, and the Japan Institute for the Control of Aging, Shizuoka-ken, Japan, to study the antioxidative activity of coffee components. GC-MS analysis of coffee extracts showed the presence of antioxidative heterocyclic compounds including furans, pyrroles, and maltol. Collectively, these provided a significant concentration of antioxidative activity that the researchers believe may have a positive effect on human health (*8*).

Table 1. Potent Odorants of Coffee Drinks Showing Differences in Their Flavor Dilution (FD) Factors Before and After Heat Processing

Peak No.	Compound	Odor Quality	FD Factor Before Heating	FD Factor After Heating
1a	Methanethiol	Putrid	1	4
15	2-Furfurylthiol	Roasty	200	40
16	Methional	Potato-like	4	1
17	Acetic acid	Sour	Nd	2
21	3-Mercapto-3-methylbutyl formate	Roasty	20	Nd
27	3-Methylbutanoic acid	Sour	Nd	4
28	2-Furfuryl methyl disulfide	Meaty	4	20
34	4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone	Caramel-like	40	200

Note: Nd, not determined.
Source: Adapted with permission from Ref. 5.

These and a host of other studies on flavor, processing, and health continue in an attempt to define and develop improved coffee quality control—which could in turn benefit the coffee production market as a whole as well as the choices available to consumers.

Nonvolatile Solutions?

Of course, one farmer's luck is another farmer's catastrophe. Purveyors of demonstrably higher-quality beans may be able to support higher prices but may also tailor the market away from those suppliers unable to produce the best coffees, whether through climate, growing costs, or simple geography. Detecting cheap adulterations or lower-quality products using GC and other analytical techniques may benefit the high-end growers but cripple those poor suppliers of the "adulterating beans," or lower-quality product.

To prevent the collapse of local economies that such a shift to higher quality would entail, USAID has established a program to help farmers who cannot switch to new forms of high-quality production. This program is designed to phase out coffee production among these individuals to different cash crops—all the while aiming to prevent the shift to growing the even more lucrative high-cash crops—coca (for cocaine) or opium poppies (for heroin).

Whatever the final outcome in terms of agrarian misery, the urban drug problem, or the flavor of one's morning "cuppa," the role of GC in the coffee crisis is likely to grow—another fascinating example of the effect of analytical technology in the global marketplace. And perhaps the improved quality that the new techniques might provide may entice consumers into that second and even third cup—thereby increasing coffee demand and helping the crisis-riddled market as a whole.

Waste Not?

Perhaps not surprisingly, if thought about, one of coffee's most notable contributions to global ecology (other than the agricultural impact of farming the coffee plant) is the presence of caffeine passed with human urine into the world's waterways. In a recent study by researchers at the Swiss Federal Research Station, Wadenswil, Switzerland, reported in *Environmental Science and Technology* (**2003,** *37,* 691–700), GC-MS analysis demonstrated that caffeine was a ubiquitous component of Swiss waterways. Lake and river water contained 6–250 ng caffeine/L, except for the most remote mountain lakes, where it was less than 2 ng/L. So noticeable was this contribution of the human race's obsession with coffee (not to mention tea and caffeine-containing pharmaceuticals) that the paper's authors suggested that caffeine could be an excellent anthropogenic marker for monitoring effluent of untreated wastewater escaping into surface waterways. They reported that human discharge of caffeine was 15.8 ± 3.8 mg/person/day, and even after wastewater treatment, a significant amount remained—0.6 ± 0.3 mg/person/day, making it an excellent potential marker of effluent flow in the environment.

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